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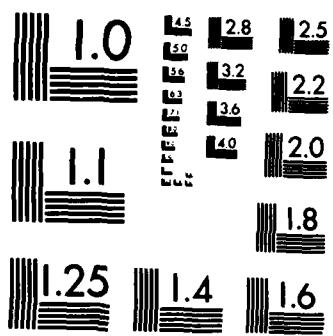
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High Performance Liquid Chromatographic Studies of the Ion Exchange
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by

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**High Performance Liquid Chromatographic Studies
of the Ion Exchange Selectivity of Nafion**

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Brief

Nafion-based HPLC columns were prepared by coating 5 μM ODS with Nafion films. Studies of the ion exchange selectivity of these columns showed that Nafion has remarkable affinity for hydrophobic cations.

Abstract

Nafion films were coated on 5 μM octadecyl-derivatized silica. HPLC columns were packed with this film-modified ODS and the ion exchange selectivity of Nafion was studied. A homologous series of organic cations was used to probe the ion exchange properties of Nafion. These studies show that Nafion has remarkable affinity for hydrophobic cations. The logs of the ion exchange selectivity coefficients for the cations of the homologous series were found to increase in a linear fashion with the molecular weight of the cation. The theoretical and practical implications of this unusual ion exchange selectivity are discussed.

INTRODUCTION

We have recently reported results of fundamental studies of ion exchange reactions involving hydrophobic cations in Nafion films at electrode surfaces (1). These studies have shown that Nafion has remarkable affinity for such cations. For example, the selectivity coefficient associated with the exchange of Na^+ with $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$) in Nafion was found to be 5.7×10^6 (1). While these and other studies (2-6) clearly show that hydrophobic interactions can play a role in determining the strength of the Nafion/counterion interaction, structural and charge differences in the counterions used made quantitative conclusions about the contribution of the hydrophobic effect difficult. Furthermore, the electrochemical isotherm method used (1,7) is extremely tedious and time consuming.

We are interested in learning more about the contribution of the hydrophobic effect to counterion binding in Nafion and other ionomers (8). It seemed likely that high performance liquid chromatography (HPLC) would prove to be a much more convenient and powerful tool for studying ion exchange reactions in these polymers. To test this hypotheses, we have used an HPLC method to study ion exchange reactions of a homologous series of alkylpyridinium ions in Nafion. We report results of these and related studies here.

EXPERIMENTAL SECTION

Apparatus. The liquid chromatograph consisted of a Spectra-Physics 8700 solvent delivery system, a Rheodyne model 7125 injection valve with a 10- μl sample loop, a Gilson Holochrome HM/HPLC UV/Visible detector, and a Linear Instruments model 500 laboratory chart recorder. The 15 cm x 4.6 mm (i.d.)

stainless steel columns (Rainin) were packed using a Haskel air driven fluid pump. The polymer was dissolved in a Parr model 4562 "Mini" Pressure Reactor.

Reagents. Tetramethylammonium bromide (TMAB) (Aldrich) was recrystallized from ethanol and water. Methylviologen (MV^{2+}) was obtained from Aldrich Chemical Co. Water was obtained from a Milli-Q water purification system, and methanol was MCB Omnisolv. The Nafion (1100 equivalent weight, EW) was obtained from E.I. du Pont de Nemours and Co. A homologous series of organic cations was prepared by allowing pyridine (Fisher Scientific Co.) to react with various linear alkyl bromides (1-bromoethane to 1-bromopentane) (Aldrich), at room temperature, for 5 days. The products were then recrystallized from an ethanol-ether solution. All other reagents were of the highest quality available and were used without further purification.

Preparation of Chromatographic Columns. A stock solution of the Nafion polymer was prepared using the procedure of Martin et al. (9). The concentration of this solution (0.34 (w/v) %) was determined by evaporating a known volume to dryness, in vacuo, and weighing the residue. A 0.01% solution was prepared from this stock solution by diluting with 50:50 ethanol-water. Octadecyl-derivatized silica (ODS) (5 μ M average diameter) and underivatized silica (Nucleosil 100-10) were obtained from Rainin. We initially attempted to coat the underivatized silica but found that Nafion would not adhere. We believe that this is because both Nafion and silica are anionic (and, therefore, electrostatically repellent) and because Nafion is hydrophobic while silica is hydrophilic. This latter point is strengthened by our observation that Nafion will not stick to glass but sticks quite nicely to dimethyldichlorosilane treated glass (10). It is of interest to note

that Kirkland has succeeded in getting a lower EW Nafion to stick to silica (11,12).

Nafion's preference for hydrophobic surfaces is further demonstrated by the fact that it will adhere to ODS; therefore, ODS was used as the substrate material. 2.5 g of 5 μ M ODS were added to 25 mL of the 0.01% Nafion solution. The solvent was evaporated from the resulting slurry by stirring in a water bath at 70°C. The modified ODS was then transferred to a vacuum oven and stored overnight at 70°C.

The quantity of Nafion on the packing material was measured using the following procedure. After packing, the column was rinsed with 200 mL of triply distilled water (flow rate = 1 mL min⁻¹). The $-SO_3^-$ sites were then quantitatively converted to the ethylpyridinium salt form by passing a large volume of a 10⁻³ M aqueous solution through the column. The column was rinsed with water until all excess ethylpyridinium was removed (absorbance returned to baseline). The ionically bound ethylpyridinium was then quantitatively eluted from the column with 0.1 TMABr in methanol. The eluant was collected, and the concentration of ethylpyridinium determined spectrophotometrically. The volume of Nafion on the ODS (the volume of the stationary phase, V_s) was calculated by multiplying the moles of sulfonate sites by the equivalent weight and dividing by the density of the Nafion (5).

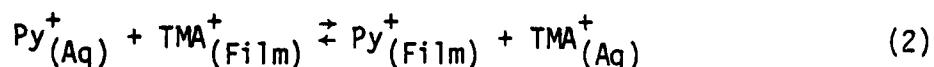
Prior to packing, both the ODS and ODS-Nafion particles were sized by adding them to 100 mls of methanol, agitating, allowing time for the majority of the particles to settle, and then drawing off the methanol, which contained fines. This process was repeated until the methanol remained relatively clear after sedimentation. Both ODS and ODS-Nafion columns were packed using the down-flow method of high pressure slurry-packing (13).

Chromatographic Conditions and Procedures. The various mobile phases were prepared by programming the Spectraphysics 8700 to mix appropriate quantities of either pure water or pure methanol with a solution of the desired salt (e.g., NaBr, TMABr, etc.). All mobile phase solvents were passed through a 0.2 μM nylon filter (Rainin), and degassed with helium prior to use. All chromatographic experiments were carried out at a flow rate of 1 mL/min, except during studies of efficiency as a function of flow rate. The columns were operated at ambient temperature ($22 \pm 1^\circ\text{C}$) and the detector was operated at 254 nm. Column void volumes were determined using concentrated aqueous NaNO_3 solutions (14).

The retention characteristics of the Nafion columns were evaluated using the series of alkylpyridinium cations as probes. The Nafion $-\text{SO}_3^-$ sites were initially in the TMA^+ salt form and TMA^+ was used as the eluant. Ion exchange partition coefficients for the alkylpyridiniums (k^{Py^+}) were calculated from the retention data as follows:

$$k^{\text{Py}^+} = k' V_M / V_S \quad (1)$$

where k' is the capacity factor (15), V_M is the mobile phase volume, and V_S is the stationary phase volume. The capacity factors were determined from the peak maxima. The ion exchange selectivity coefficient ($k_{\text{TMA}^+}^{\text{Py}^+}$) for the exchange of TMA^+ with an alkylpyridinium (Py^+ , i.e., the reaction)



is given by:

$$K_{\text{TMA}^+}^{\text{Py}^+} = [\text{Py}^+]_{(\text{Film})} [\text{TMA}^+]_{(\text{Aq})} / [\text{Py}^+]_{(\text{Aq})} [\text{TMA}^+]_{(\text{Film})} \quad (3)$$

Equation (1) may be substituted into equation (3) to give,

$$K_{TMA^+}^{Py^+} = k^{Py^+} [TMA^+]_{(Aq)} / [TMA^+]_{(Film)} \quad (4)$$

Because the concentration of TMA^+ in the aqueous phase was high (1 M), it was assumed to be constant (16). Furthermore, by injecting small quantities of the alkylpyridiniums, the average number of sites occupied by an alkylpyridinium can be kept negligibly small (16) making $[TMA^+]_{(Film)}$ just the capacity of the column divided by V_S . These considerations simplify calculations of $K_{TMA^+}^{Py^+}$ (equation (4)). All ODS-Nafion columns prepared showed analogous retention characteristics. The results presented here were obtained on a single column which contained 2.6 moles of $-SO_3^-$ sites, $V_S = 1.8 \mu L$, $V_M = 1.6 \text{ mL}$. The selectivity coefficient showed no significant variation with concentration of the alkylpyridinium when alkylpyridinium concentration varied over the range 5×10^{-5} to $5 \times 10^{-4} \text{ M}$. A gradual decrease in K was observed at concentrations higher than ca. 10^{-3} M .

Extremely long retention volumes were obtained when aqueous solutions of inorganic salts were used as the eluants for the alkylpyridiniums. Because of excessive band broadening, detection of such highly retained solutes proved difficult. For this reason, we adopted a convention of waiting 35 min. for a band to elute. If no peak was detected after this time interval, the experiment was terminated and the solute was flushed from the column with a solution of NaBr in methanol.

Efficiencies of both the ODS and ODS-Nafion columns were evaluated by determining numbers of theoretical plates (17) and asymmetry factors (18). Phenol, eluted with 50:50 methanol-water and propylpyridinium eluted with aqueous 1 M TMABr were used to evaluate plate numbers for the ODS and ODS-Nafion columns, respectively. Ethylpyridinium eluted with 0.95 M TMABr

was used to determine the asymmetry factors.

RESULTS AND DISCUSSION

General Retention Characteristics of ODS-Nafion. If partition or ion exchange selectivity coefficients are to be calculated from retention data, the void volume, V_M , must first be measured. While an accurate determination of V_M is never a trivial matter (14), because Nafion has both reversed phase and ion exchange characteristics, measuring V_M for Nafion-based columns is particularly difficult. Obviously, cations and molecules which can engage in hydrophobic interactions with Nafion will produce spuriously large V_M values. Furthermore, if an anion is used to determine V_M , low values could be obtained due to electrostatic exclusion of the anion from portions of the mobile phase. We have observed this co-ion exclusion effect when eluting low concentrations of p-toluenesulfonate from the Nafion-based columns (*vide infra*).

It is important to note that co-ion exclusion decreases and eventually becomes negligible as the concentration of the co-ion in the mobile phase increases (19). Because a small inorganic anion at high concentrations will have no hydrophobic interaction and no electrostatic interaction (either attractive or repulsive) with Nafion, such an anion seems to be the ideal candidate for determination of V_M for Nafion-based HPLC columns. We have used aqueous NaNO_3 solutions (14) (0.3 to 1.0 M) to determine V_M . No variation in V_M with concentration of NaNO_3 was seen over this high concentration range.

Comparisons of retention volumes, V_R 's, for the alkylpyridiniums on ODS columns with V_R 's on ODS-Nafion clearly showed that the Nafion coating drastically altered the retention characteristics of ODS. For example,

when 100% methanol was used as the eluant, propylpyridinium had a V_R of 3.6 mL on an ODS column and a V_R of greater than 35 mL on the ODS-Nafion column. If, however, 95% methanol-5% 1 M TMABr was used, propylpyridinium was eluted from the ODS-Nafion column in 2.8 mL. Similar results were obtained with the other pyridiniums. Because the pyridiniums would not elute from the ODS-Nafion column (in under 35 min.) unless salt was added to the mobile phase, these studies strongly suggested that ODS-Nafion was, as expected, acting as a cation exchange material. This conclusion is supported by the fact that both anions and neutrals could be easily eluted from ODS-Nafion columns with pure methanol. For example, V_R 's for benzene and p-toluenesulfonate (PTS) are 2.3 and 1.4 mL, respectively. Note that V_R for PTS is less than the measured V_M (1.6 mL). As noted above, this is undoubtedly due to exclusion of this anion from portions of the mobile phase.

The importance of hydrophobic interactions became apparent during attempts to elute the pyridiniums with 100% aqueous mobile phases. Salts containing inorganic cations (e.g., Na^+ , K^+) would not elute the larger pyridiniums from the ODS-Nafion column (in under 35 min.), while salts containing organic cations (e.g., TMA^+ , tetraethylammonium) would. For example, V_R for propylpyridinium using aqueous 0.1 M TMABr as the eluant was 5.1 mL while V_R using aqueous 0.1 M NaBr was greater than 35 mL. In general, with aqueous mobile phases, only an organic cation could elute an organic cation from the ODS-Nafion column. In contrast, in pure methanol mobile phases, nearly any cation (e.g., Na^+ , K^+ , TMA^+) could elute the pyridiniums. (For example, V_R for ethylpyridinium was 4.5 mL when methanolic 0.1 M KBr was used as the eluant). These observations corroborate prior conclusions (1,3-6) regarding the importance of hydrophobic interactions to counterion binding in Nafion (vide infra).

The preceding studies indicated that Nafion on ODS displayed solubility and ion exchange properties similar to bulk Nafion membranes (4) and to ca. 1 to 2 μM thick Nafion films on electrode surfaces (1). This is an important observation because despite its speed and convenience, this HPLC procedure would be of little value if data obtained were not representative of the inherent properties of the polymer being studied. To further test the fidelity of the method, ion exchange selectivity coefficients for the replacement of Na^+ with MV^{2+} , i.e. $K_{\text{Na}}^{\text{MV}^{2+}}$, were determined. In our electrochemical isotherm study (1), ion exchange selectivity coefficients were reported in terms of mole fractions rather than concentrations of ions in the polymer phase. Converting the value of $K_{\text{Na}}^{\text{MV}^{2+}}$ obtained (1) to the corresponding concentration-based value produces $K_{\text{Na}}^{\text{MV}^{2+}} = 4.0 (\pm 0.2) \times 10^3$. With the HPLC procedure the value of $K_{\text{Na}}^{\text{MV}^{2+}}$ obtained varied with the molarity of (aqueous) NaBr used as the eluent decreasing from $4.64 (\pm 0.05) \times 10^3$ (2 M NaBr) to $1.97 (\pm 0.05) \times 10^3$ (1 M NaBr). This variation in $K_{\text{Na}}^{\text{MV}^{2+}}$ with ionic strength is not surprising since these are selectivity coefficients (equation 3) and not thermodynamic selectivity constants (20,21). The agreement between the two methods is excellent.

Ion Exchange Selectivity Coefficients. Aqueous ion exchange selectivity coefficients (vs. TMA^+) for the various alkylpyridinium ions are shown in Table 1. It is first important to note the immense sizes of these selectivity coefficients. Yeager and Steck (22) obtained ion exchange selectivity coefficients for various monovalent, inorganic ions in Nafion membranes; the largest selectivity coefficient observed was $K_{\text{H}^+}^{\text{Cs}^+}$ which had a value of 9.1 (22). The selectivity coefficients for the hydrophobic ions studied here are from 2 to 3 orders of magnitude larger than this.

Furthermore, the selectivity coefficients shown in Table I are measured vs. TMA^+ whereas Yeager's (22) are measured vs. H^+ . Because inorganic ions will not even elute the larger pyridiniums from the Nafion column (in under 35 min.), values of $k_{\text{H}^+}^{\text{Py}^+}$, if they could be directly measured, would be even larger than the values (vs. TMA^+) reported here. These data are very clear evidence that Nafion shows tremendous preference for hydrophobic cations relative to simple inorganic cations (1).

The role of hydrophobic interactions in the binding of counterions to Nafion is more dramatically demonstrated, and placed on more quantitative terms, through a plot of $\log k_{\text{TMA}^+}^{\text{Py}^+}$ vs. number of carbon atoms in the pyridinium. This "free energy plot" (23) is linear (slope = 0.380, correlation coefficient = 0.996), demonstrating that each increment of molecular bulk (i.e., hydrophobicity) adds an increment of thermodynamic driving force to the ion exchange reaction. From the slope of this line, it can be calculated that each additional carbon contributes an additional -0.518 kCal/mole to the standard free energy change for the ion exchange reaction of an alkylpyridinium.

As noted by Rothbart (24), equation 4 can be rearranged as follows

$$\log k^{\text{Py}^+} = \log[\text{TMA}^+]_{(\text{Film})} + \log k_{\text{TMA}^+}^{\text{Py}^+} - \log[\text{TMA}^+]_{(\text{Aq})} \quad (5)$$

If, over a given eluent concentration range, the ion exchange selectivity coefficient is constant, a plot of $\log k^{\text{Py}^+}$ vs. $-\log[\text{eluent}]$ is linear and the slope is equal to the charge on the exchanging ion (24). Such a plot can be used to confirm that an ion exchange reaction is, indeed, occurring and to assess the stoichiometry of this reaction (24). As noted above, ion exchange selectivity coefficients for the Nafion-based columns are not constant over the eluent concentration ranges which produce manageable

retention volumes. The nonconstancy of $K_{TMA}^{Py^+}$ is illustrated by the data in Table II. A plot of $\log k^{Py^+}$ vs. $-\log[\text{eluent}]$ is of little value for this system.

Equation (5) may be rearranged as follows

$$\log k^{Py^+} = \log[TMA^+]_{(\text{Film})} + \log \frac{K_{TMA}^{Py^+}}{[TMA^+]_{\text{Aq}}} \quad (6)$$

Thus, a plot of $\log k^{Py^+}$ vs. $\log(K_{TMA}^{Py^+}/[TMA^+]_{\text{Aq}})$ should be linear with a slope of 1.0. Such a plot is analogous to Rothbart's (24) (equation (5)) but compensates for the variation in $K_{TMA}^{Py^+}$ with $[TMA^+]_{\text{Aq}}$. When the data in Table II are plotted according to equation (6), a line (correlation coefficient = 0.9996, intercept = 0.224) with a slope of 0.98 is obtained. The close agreement between the predicted and experimental slopes confirms that the Nafion-based columns are acting as cation exchange materials.

Efficiency and Resolution. Figure 1 shows a typical chromatogram for a mixture of three of the alkylpyridinium ions on an ODS-Nafion column. Note that these pyridiniums differ in molecular weight by only one methylene group yet good separation is obtained. These data suggest that Nafion-based HPLC columns should be useful for separations of organic cations. Indeed, Kirkland (11,12) has demonstrated that a number of separations of practical interest can be performed on HPLC columns prepared from a low EW version of Nafion. It is important to note that these low EW Nafion films are soluble in ethanol and other organic solvents whereas high EW Nafion films can be made insoluble (25) in all solvents (at temperatures below ca. 200°C). Therefore, HPLC columns prepared from high EW Nafion have the advantage of being usable in any desired solvent system. Furthermore, a comparison (1) of ion exchange data for low (2) and high (1) EW Nafion suggests that low EW Nafion has

a much lower affinity for hydrophobic cations.

Pronounced peak tailing is observed in the chromatogram shown in Figure 1. Asymmetry factors of about 11 were typically obtained on ODS-Nafion whereas asymmetry factors of about 6 were obtained on our homepacked ODS columns. The poorer symmetry observed with the ODS-Nafion columns could be caused by either thermodynamic (i.e., non-linear isotherm), diffusive or kinetic problems. Our studies of ion exchange in Nafion-based chemically modified electrodes have shown that the partition isotherm for an organic cation begins to bend over when about 1% of the available $-SO_3^-$ sites in the Nafion film are occupied by this cation (1). For this reason, our initial assumption was that the peak tailing was the result of isotherm non-linearity. However, peak tailing is observed under conditions where calculations (15) show that less than 0.001% of the $-SO_3^-$ sites are occupied by the alkylpyridiniums (i.e., very low sample concentrations). Therefore, the enhanced asymmetry for the ODS-Nafion columns appears to be dynamic in origin. We are currently studying the effects of the solvent and the film thickness on the column dynamics.

A plot of height equivalent to a theoretical plate (HETP) vs. flow rate for an ODS-Nafion column is shown in Figure 2. The typical (26) increase in HETP with flow rate is observed. However, as was also observed by Kirkland (11) for columns prepared from the low EW Nafion, the HETP curve exhibits a pronounced flattening at higher flow rates. This means that higher flow rates may be used without significant loss of efficiency (11).

CONCLUSIONS

These studies have shown that an HPLC procedure can be used as a convenient and rapid tool for studying ion exchange reactions in ionomers. The ion exchange data obtained have been shown to be the same (both

qualitatively and quantitatively) as data obtained from a tedious and time consuming isotherm method (1). The isotherm data were obtained from Nafion films ranging from 1 to 2 μM in thickness which had up to 40% of their $-\text{SO}_3^-$ sites occupied by the exchanging ion. Clearly, the ion exchange selectivity coefficients in this case describe bulk film rather than surface processes (1). In contrast, in the current study the loading of the exchanging ion was kept below 1% of the available $-\text{SO}_3^-$ sites and, while the film thicknesses are unknown, the rather low capacities of these columns suggest that these films are very thin. These are interesting points because they suggest that the ion exchange data in the HPLC experiment might reflect surface rather than bulk processes; future studies will assess how well ion exchange data for columns like those described here conform to current theories (27) of surface ion exchange processes. If the data obtained here do reflect surface rather than bulk film ion exchange, the thermodynamics of these processes must be very similar.

The results obtained corroborate earlier conclusions regarding the importance of hydrophobic interactions to counterion binding in Nafion (1,3-6). Conventional ion exchange resins do not show Nafion's remarkable affinity for hydrophobic counterions (1,28). For example, Gregor and Bregman studied ion exchange reactions of a variety of alkyl and phenyl-alkylammonium ions in sulfonated polystyrene resins (28); these resins contained from about 1 to 35% cross-linking. While selectivity coefficients as large as about 20 were observed (28), none of the resins studied produced selectivity coefficients as large as those shown in Table 1 or reported in our previous publication (1). We are currently using the HPLC method in studies aimed at ascertaining why Nafion's ion exchange characteristics are so unusual.

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Table I. Ion exchange selectivity coefficients on ODS-Nafion column.^a

Pyridinium Ion	$K_{TMA^+}^{Py^+}$
Ethylpyridinium	4.3×10^2
Propylpyridinium	8.5×10^2
Butylpyridinium	2.1×10^3
Pentylpyridinium	5.7×10^3

^aMobile phase = 0.95 M aqueous TMABr, flow rate = 1 mL/min, 10 μ L samples of 10^{-3} M aqueous pyridinium solution injected.

Table II. Dependence of $K_{TMA^+}^{Py^+}$, for ethylpyridinium, on concentration of TMA^+ for the Nafion-based columns.

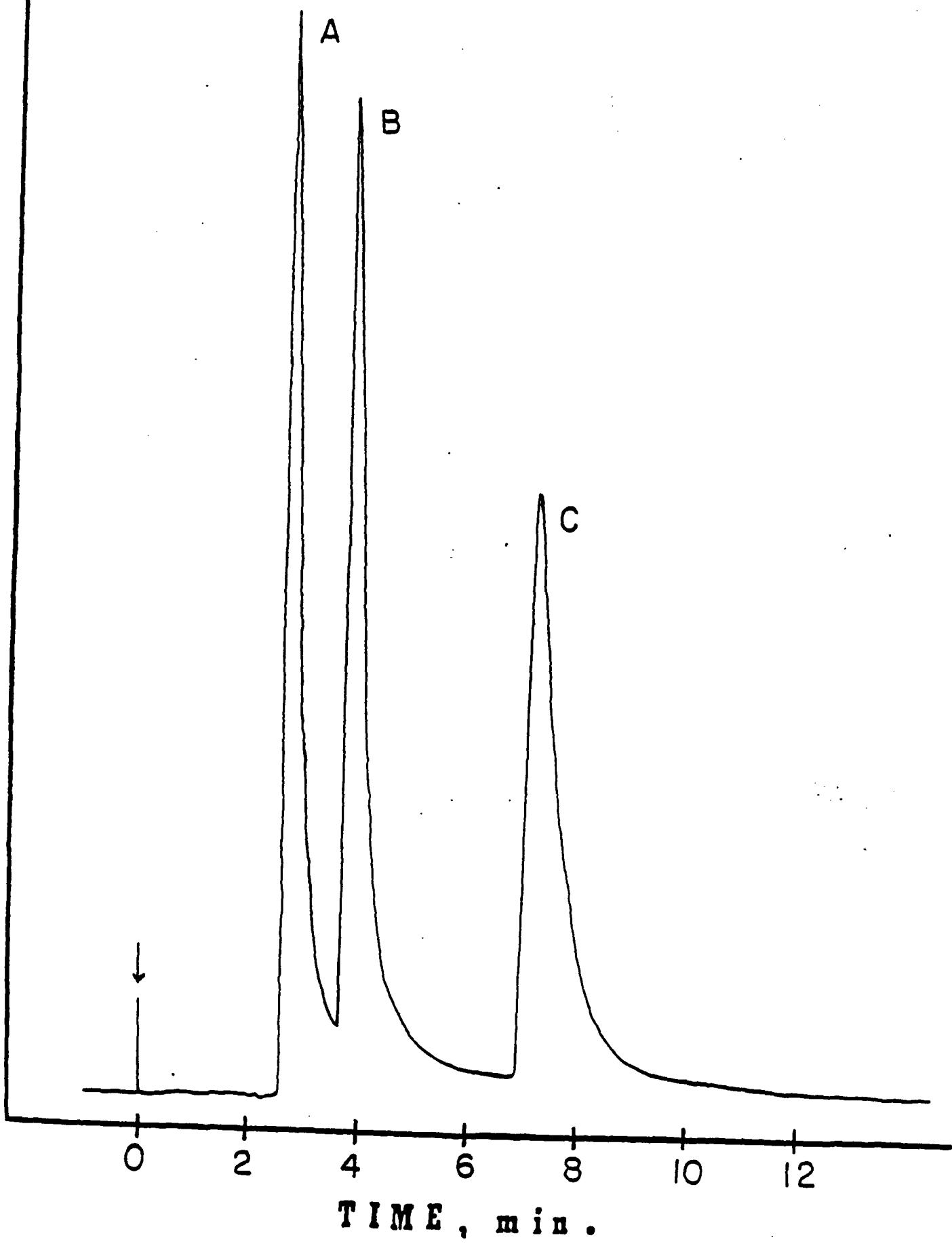
[TMA ⁺]	k^{Py^+}	$K_{TMA^+}^{Py^+}$
0.1	1.88×10^3	131
0.2	1.37×10^3	191
0.3	1.14×10^3	239
0.4	1.03×10^3	286
0.5	9.29×10^2	323
0.6	8.38×10^2	350
0.8	7.30×10^2	406

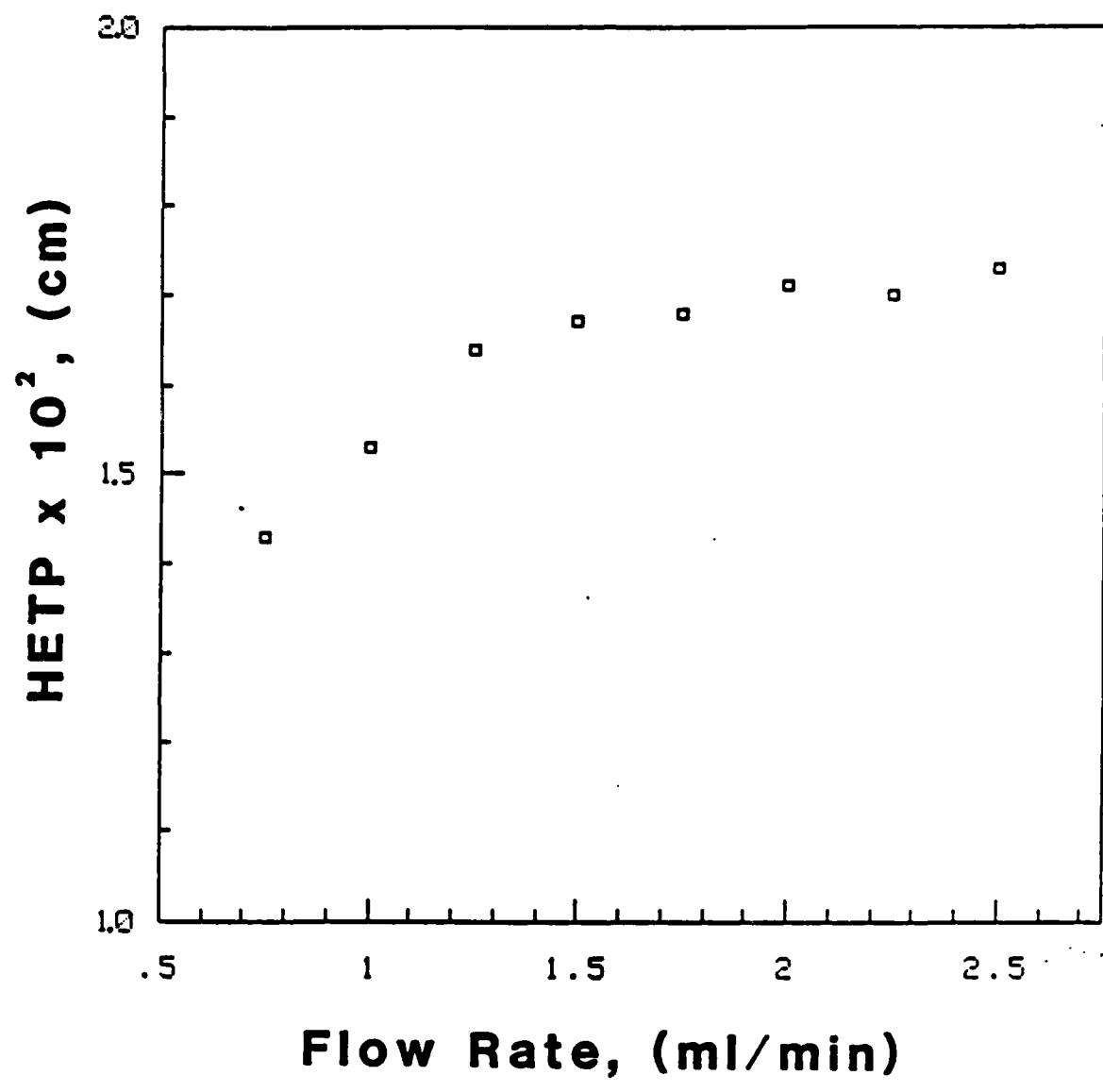
Figure Captions

Figure 1. Chromatogram for a mixture of A, ethylpyridinium; B, propylpyridinium; C, butylpyridinium on ODS-Nafion. All constituents 10^{-3} M (aqueous). Eluant is 1.0 M TMABr aqueous. Flow rate = 1 mL min $^{-1}$.

Figure 2. Plot of HETP vs. flow rate for an ODS-Nafion column. Solute is propylpyridinium. Eluant is 0.95 M TMABr.

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